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July 14, 2004

21st JANNAF S&EPS Meeting
Seattle, WA, United States
July 26, 2004 through July 29, 2004

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Recent Progress on the Conversion of Surplus Picric Acid/Explosive D to Higher Value Products

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Article for the 21th JANNAF S&EPS Meeting

Seattle, Washington

July 26-29, 2004

This work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

ABSTRACT

The global demilitarization of nuclear and conventional munitions is producing millions of pounds of surplus energetic materials. Historically, energetic materials (high explosives, propellants, and pyrotechnics) have been disposed of by open burning/open detonation (OB/OD). The use of OB/OD is becoming unacceptable due to public concerns and increasingly stringent environmental regulations. Clearly, there is a great need to develop environmentally sound and cost-effective alternatives to OB/OD. The conversion of surplus picric acid and/or ammonium picrate (Explosive D) to 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) has been subject of extensive process development studies at Lawrence Livermore National Laboratory (LLNL). LLNL, under the direction and sponsorship of the U.S. Army Defense Ammunition Center (DAC), is developing a process for the conversion of picric acid to TATB on a larger scale. In FY 03, a 10 g per batch process was developed with good results. Development for an one pound per batch system is required as part of overall scale up process for producing TATB from the surplus feedstocks.

INTRODUCTION

Our objective has been to develop new and innovative solutions for the disposal of surplus energetic materials. Disposal through open burning/open detonation (OB/OD) is less attractive today due to environmental, cost and safety concerns. We have examined various scenarios using military high explosives as raw materials and have found that nitroarene explosives such as Explosive D (ammonium picrate) and TNT (2,4,6- trinitrotoluene) can serve as feedstocks for a variety of higher value products.¹⁻⁴ After a review of chemical conversion activities by earlier workers, we will discuss the current use of nitroarene explosives to prepare higher value explosives.

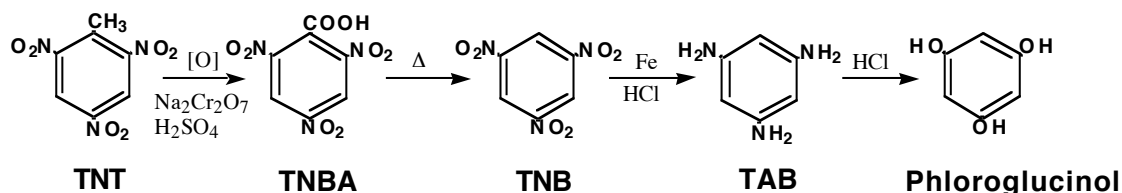


Figure 1. Commercial production of phloroglucinol from TNT.

EARLY CHEMICAL CONVERSION STUDIES

The chemical conversion of surplus energetic materials must yield commercially viable products. The conversion of TNT to phloroglucinol (1,3,5-trihydroxybenzene) was developed at the end of World War II as a means of using up the large stockpiles of TNT on hand (Figure 1).⁵ Unfortunately, this process was discontinued in the USA in the 1970s due to environmental problems associated with the waste disposal of acid liquors, iron, chromium and ammonium salts. Phloroglucinol is used in the pharmaceutical, cosmetics, textile-dyeing and photographic industries and is currently priced at \$50/lb (bulk quantities).

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Germany acquired three hundred thousand tons of old and substandard munitions when the former German Democratic Republic (GDR) was reunited with the Federal Republic of Germany (FRG) in 1989. Wanninger has discussed the disposal program that was undertaken in the early 1990s.^{6,7} It was concluded that reformulation of the surplus energetic materials for both civilian and military applications was infeasible. Chemical conversions were explored, but no commercially attractive products were produced. Destruction by OB/OD and biodegradation was ruled out for environmental and economic reasons. Incineration of the surplus munitions in rotary kilns was concluded to be the most efficient mode of destruction that also complied with German air quality standards. Unfortunately, the disposal options available today were not explored in Germany in the early 1990s. For example, a recent NATO advanced research workshop was convened to discuss the successful and extensive use of surplus explosives in

mining and other applications.⁸ The chemical conversion of surplus energetic materials, a somewhat more challenging enterprise, will now be discussed.

TATB

TATB (1,3,5-triamino-2,4,6-trinitrobenzene) is a reasonably powerful high explosive whose thermal and shock stability is considerably greater than that of any other known material of comparable energy.⁹ It is used in military applications because of its significant insensitivity to thermal and shock environments.¹⁰ In the civilian sector, Schlumberger has designed perforating guns containing TATB for deep oil well explorations where heat-insensitive explosives are required.¹¹ TATB is also used to produce benzenehexamine, an intermediate in the synthesis of new, advanced materials.¹²⁻¹⁶ In addition, the use of TATB to prepare components of liquid crystals for use in display devices is the subject of a German patent.¹⁷ TATB had been priced at \$20 to \$50 per pound before industrial production ceased in the U.S. at the end of the 1980s. TATB is currently available to customers outside of the Department of Energy (DOE) for \geq \$100 per pound.

SURVEY OF TATB SYNTHESSES

TATB has not been manufactured in the USA for over 10 years. TATB was formerly produced using the synthesis developed by Benziger (Figure 2).^{18,19} The relatively expensive and domestically unavailable 1,3,5-trichlorobenzene (TCB)

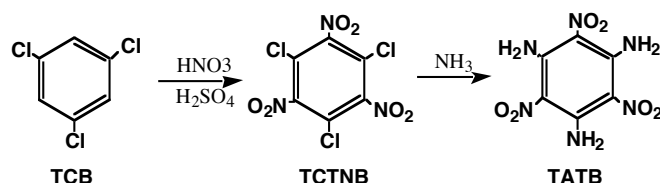
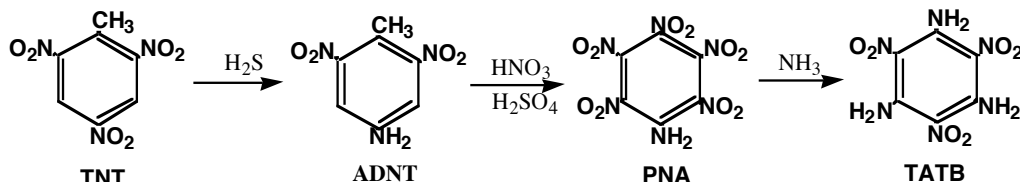


Figure 2. Benziger synthesis of TATB.

is nitrated to give 2,4,6-trichloro-1,3,5-trinitrobenzene (TCTNB), which is then aminated to yield TATB. Elevated temperatures (150°C) are required for both reactions. The major impurity encountered in this process is ammonium chloride. The inclusion of 2.5% water during the amination step significantly reduces the ammonium chloride content of the TATB. Low levels of chlorinated organic impurities have also been identified.²⁰ There is a desire to develop a synthesis of TATB that does not require such harsh reaction conditions (elevated temperature, strong acid). In addition, there is mounting environmental pressure to abandon the use of halocarbons such as TCB in favor of more benign and “greener” feedstocks in industrial processes.^{21,22}

Atkins and coworkers described a conversion of TNT to TATB^{23,24} with the goal of developing a less costly production of TATB (Figure 3). The conversion of TNT to TATB proceeds in 44% overall yield. Although all of the reactants are relatively inexpensive, the cost of pollution abatement ultimately prevented



the industrial scale-up of this process.

Figure 3. Atkins synthesis of TATB from TNT.

Wolff and Limbach have described the synthesis of ^{15}N -labelled TATB for use in the preparation of ^{15}N -labelled benzenehexamine derivatives (Figure 4).²⁵ Due to the relatively high cost of ^{15}N -labeled precursors ($^{15}\text{NH}_4\text{Cl}$, $\text{Na}^{15}\text{NO}_3$), syntheses that work well with unlabeled materials (Figure 2)^{18,19} can become excessively expensive with labeled compounds. The major obstacle in this route to TATB is the cost of phloroglucinol at \$50/lb (*vide supra*, Figure 1) which offers no economic advantage over the Benziger process using TCB as starting material (Figure 2).

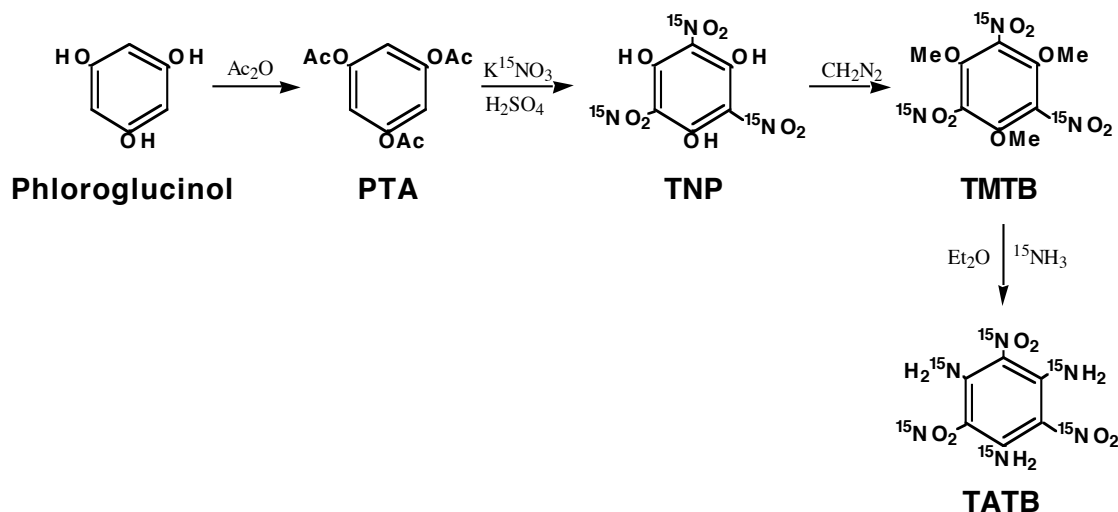


Figure 4. Conversion of phloroglucinol to ^{15}N -labelled TATB.

PROPOSED CONVERSION OF NITROARENES TO TATB

There is a definite need for a new production of TATB. We and BWXT Pantex (Amarillo, TX) have been tasked by the Advanced Development and Production Technology (ADAPT) program of DOE to develop a new production of TATB. The new production must be less expensive and more environmentally benign than the previously used processes described above. Our ultimate goal is to develop a versatile production of TATB that goes beyond the completion of demilitarization programs. The proposed production will use feedstocks from either demilitarization inventories or suppliers of commodity chemicals. A process that can utilize Explosive D and TNT (surplus nitroarene explosives) as well as picric acid and 4-nitroaniline (commodity chemicals) as starting materials is outlined in Figure 5. At the outset of this study, we found the chemistry available for the conversion of starting materials to the appropriate nitroarene intermediates marginally acceptable at best with respect to cost, safety and environmental impact. The greatest technical challenge, however, was to develop a conversion of nitroarene intermediates to TATB that precluded the use of haloarene compounds.

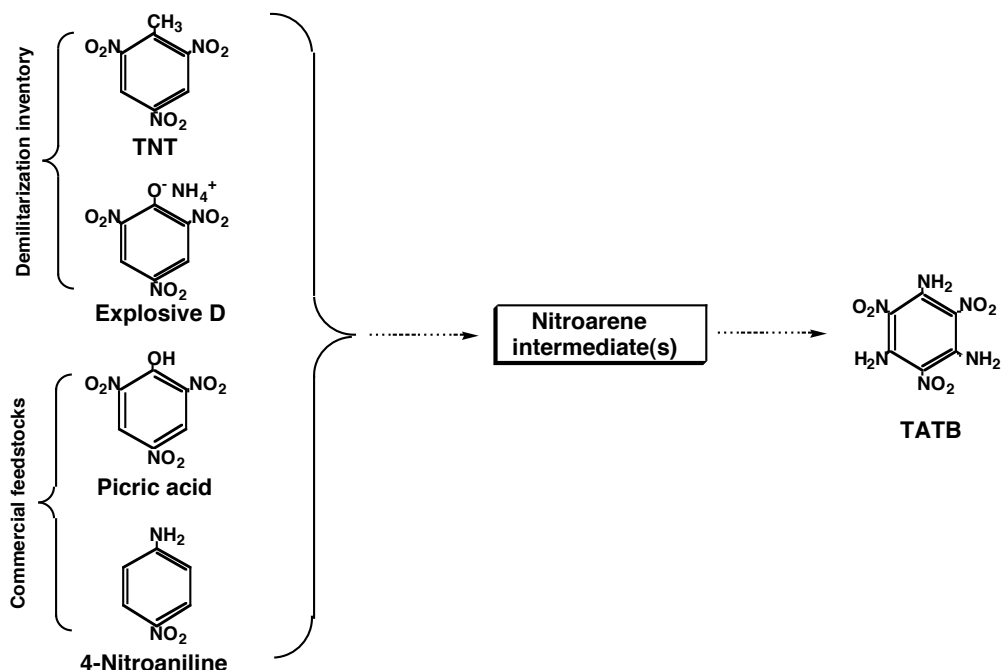


Figure 5. Proposed production of TATB utilizing either surplus explosives or commodity chemicals.

VICARIOUS NUCLEOPHILIC SUBSTITUTION (VNS) OF HYDROGEN

Vicarious nucleophilic substitution (VNS) of hydrogen is a well-established procedure for the introduction of carbon nucleophiles into electrophilic aromatic rings.^{26,27} The reaction involves the addition of a carbanion

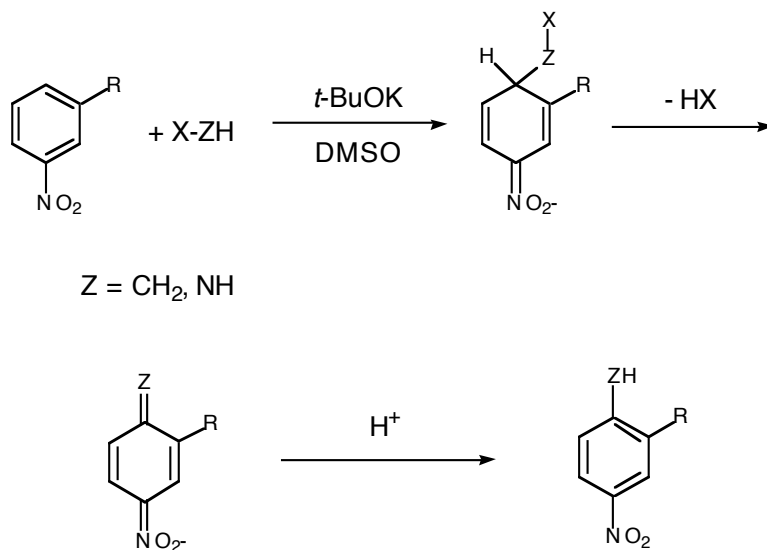


Figure 6. Vicarious nucleophilic substitution of hydrogen.

bearing a leaving group (X) to an electrophilic aromatic ring and subsequent rearomatization by loss of the leaving group through elimination as HX (Figure 6, $Z = \text{CH}_2$). This reaction has been applied to a wide variety of nitroarenes and nitro-substituted heterocycles.²⁷ By analogy, VNS reactions can also take place with amine nucleophiles.

Such reagents are of the common form X-NH₂, where X is an auxiliary group capable of stabilizing a negative charge, thus driving rearomatization of the sigma-intermediate adduct (Figure 6, Z = NH). An early example of amination by VNS of hydrogen was provided by Meisenheimer and Patzig who reacted 1,3-dinitrobenzene with hydroxylamine in the presence of strong base and methanol to yield 1,3-diamino-2,4-dinitrobenzene.²⁸ This reaction was reinvestigated by Norris and Chafin in 1985, who employed *hydroxylamine in water* to convert 4,6-dinitrobenzofuroxan (DNBF) to 5,7-diamino-4,6-dinitrobenzofuroxan (CL-14)(Figure 7).²⁹ This finding is intriguing as virtually all VNS reactions are run in anhydrous organic solvents with the exclusion of moisture.²⁶ The use of water, the ultimate “green” solvent, in a chemical reaction greatly reduces the cost of the reaction and also provides a more environmentally benign chemistry. Unfortunately, the conditions

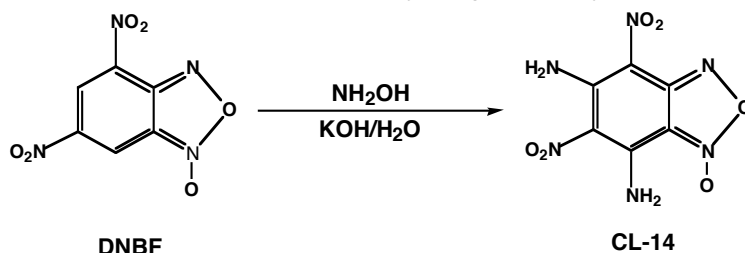


Figure 7. VNS amination of DNBF to CL-14.

used to produce CL-14 (Figure 7) did not work for the conversion of picramide to TATB (Figure 8). DATB (1,3-diamino-2,4,6-trinitrobenzene) was obtained in a low yield (16%) after removal of unreacted picramide.

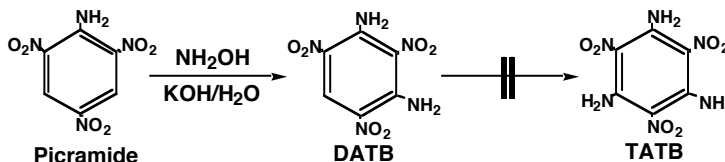


Figure 8. Reaction of picramide with hydroxylamine in aqueous base.

The reaction of picramide with hydroxylamine or its O-alkyl derivatives in NaOMe/DMSO never yielded more than trace quantities of TATB at room temperature. Recently, a number of more active aminating reagents such as 4-amino-1,2,4-triazole³⁰ and substituted sulfenamides³¹ have been developed. These reagents were designed to be good nucleophiles that easily add to electrophilic aromatic rings and also possess good leaving groups (Figure 6, X).

USE OF 1,1,1-TRIMETHYLHYDRAZINIUM IODIDE (TMHI) AS A VNS REAGENT

We were intrigued by the announcement in 1995 that Russia was intending to dispose of 30,000 metric tons of liquid rocket propellant (1,1-dimethylhydrazine, unsym-metrical dimethylhydrazine, UDMH) originally prepared for use in intercontinental ballistic missiles.³² We alkylated UDMH with methyl iodide to provide 1,1,1-trimethylhydrazinium iodide (TMHI)³³ which we evaluated as a VNS aminating reagent. Although quaternary hydrazinium compounds have been known for over one hundred years,^{34,35} they have not been employed as VNS reagents. We reasoned that TMHI would be sufficiently nucleophilic to substitute into nitro-substituted aromatic rings but would be superior to the examples described above because the leaving group would be the neutral trimethylamine instead of a stabilized anionic species. In addition, there is a possibility that the hydrazinium halide would react with base to form the neutral ylide species, [(CH₃)₃N⁺-NH⁻], which may be the reactive species in the amination process. Indeed, when TMHI was reacted with various nitro-substituted aromatics the amino functionality was introduced in good to excellent yields. We found that the number of amino-groups which may be added to the electrophilic aromatic ring is equal to the number of nitro groups present on the ring.

A study of product yields and distribution of various 3-substituted nitrobenzene

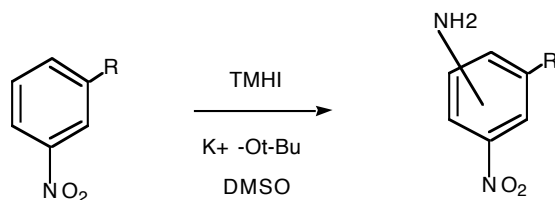


Figure 9. Amination of 3-substituted nitroaromatics.

derivatives was performed using TMHI (Figure 9).³⁶ The results of our study were compared with the findings reported for 4-amino-1,2,4-triazole (ATA).³⁰ ATA was found to be regioselective, giving substitution exclusively para- to the nitro group. TMHI gave all possible product isomers thereby showing no selectivity but presumably greater reactivity. Picramide reacts with TMHI in dimethylsulfoxide in the presence of strong base (NaOMe or KOt-Bu) at room temperature (3 h) to yield, depending on the quantity of TMHI used, either DATB or TATB and trimethylamine (TMA) (Figure 10).³⁷ Picramide also reacts with ATA in dimethylsulfoxide in the presence of strong base (NaOMe or KOt-Bu) at a slower rate (24 h) to yield either DATB or TATB, depending on the quantity of ATA used.³⁸

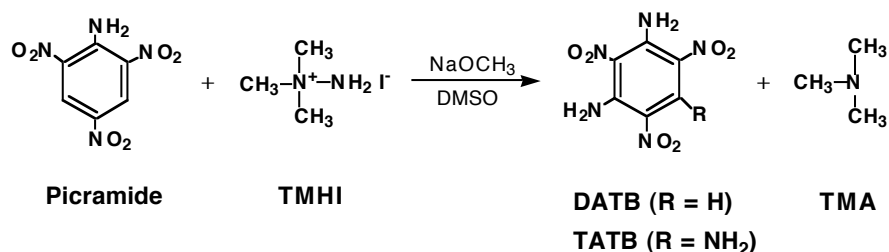


Figure 10. Reaction of picramide with TMHI.

In theory, the TMA released from the reaction of picramide with TMHI (Figure 10) can be used to regenerate VNS aminating reagent through the reaction of TMA with chloramine to yield 1,1,1-trimethylhydrazinium chloride (TMHCl).³⁵ TMHCl and TMHI, as expected, serve equally well as reagents for the nucleophilic aminations of nitroarenes.

CONVERSION OF EXPLOSIVE D TO PICRAMIDE

We have described efficient conversions of picramide (2,4,6-trinitroaniline) and TNB (1,3,5-trinitrobenzene) to TATB using VNS chemistry.³⁷⁻³⁹ Our large-scale synthesis of TATB has been designed so that either surplus energetic materials (Explosive D, TNT) or inexpensive, commercially available chemicals (picric acid, 4-nitroaniline) can be used to make the necessary starting materials (picramide, TNB). Several million pounds of Explosive D (ammonium picrate) are available for disposal in the USA. Ammonium picrate can be converted to picramide by the pathways shown in Figure 11. There is one report describing the direct conversion of picric acid to picramide.⁴⁰ Molten picric acid and urea were heated at 173°C for 36 hours to produce a mixture of picramide, urea and cyanuric acid. Removal of the urea and cyanuric acid by extractions with the appropriate solvents (water, acetone) afforded picramide in 88% yield. This procedure has major drawbacks, as molten picric acid, especially at such an elevated temperature (173°C), creates a serious explosive hazard. Furthermore, the picramide is produced as a solid glass product that cannot be safely and efficiently removed from an industrial scale reactor. What about the direct conversion of Explosive D to picramide (Figure 11, dotted arrow)? We have not found any reports in the chemical literature describing such a conversion. There are suggestions, however, that the reaction of Explosive D with urea at elevated temperature has been attempted and little or no picramide was produced.⁴¹ The reaction of picric acid and urea was reinvestigated and conditions were discovered that promoted the reaction of either Explosive D or picric acid with urea to provide picramide. Good yields (>90%) were obtained irrespective of the starting material. In each case, however, cyanuric acid was present as an unwanted by-product formed from excess urea in the reaction mixture. We have recently developed proprietary conditions under which both Explosive D and picric acid are directly converted to picramide (>90%) without the formation of cyanuric acid.⁴²

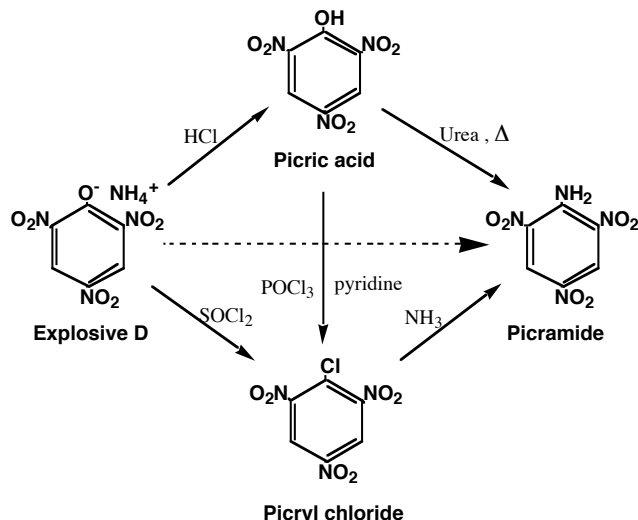


Figure 11. Pathways to picramide from Explosive D.

CONVERSION OF TNT TO TNB AND TATB

TNT may replace Explosive D as a chemical feedstock as the existing inventory of Explosive D (5 million pounds) will eventually be consumed by demilitarization through either resource recovery and reuse (R^3) or destruction activities. In addition, there are no future military requirements for the production or use of Explosive D. On the other hand, TNT remains an important military explosive. There are future requirements for a less polluting production of TNT as well as viable R^3 programs when demilitarization is required.

TNB is a key intermediate in the conversion of TNT to TATB that employs VNS chemistry (Figure 12). TNB is readily obtained in high yield from the thermal

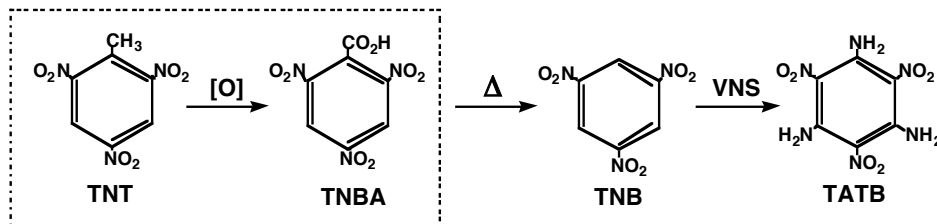


Figure 12. Conversion of TNT to TNB and VNS production of TATB.

decarboxylation of TNBA. (Figure 1).⁵ The technical challenge is to effect the oxidation of TNT to TNBA (Figure 12, dotted box) in an environmentally acceptable manner. The industrial conversion of TNT to TNBA, a key step in the production of phloroglucinol,⁵ was discontinued in the USA in the 1970s due to problems associated with the waste disposal of acid liquors and chromium salts.

TOWARDS A VERSATILE PRODUCTION OF TATB

The information provided in the previous sections and published reports³⁶⁻³⁹ indicates that we are closing in on our goal of a versatile production of TATB utilizing either surplus explosives or commodity chemicals (Figure 13). Feedstocks from both demilitarization inventories (Explosive D, TNT) and/or commercial sources (4-nitroaniline, picric acid) are employed. The four feedstocks are converted to two intermediates (picramide, 1,3,5-trinitrobenzene) which are then transformed to TATB using VNS chemistry. To date, the most extensively used feedstock in our TATB studies has been 4-nitroaniline. 4-Nitroaniline is readily

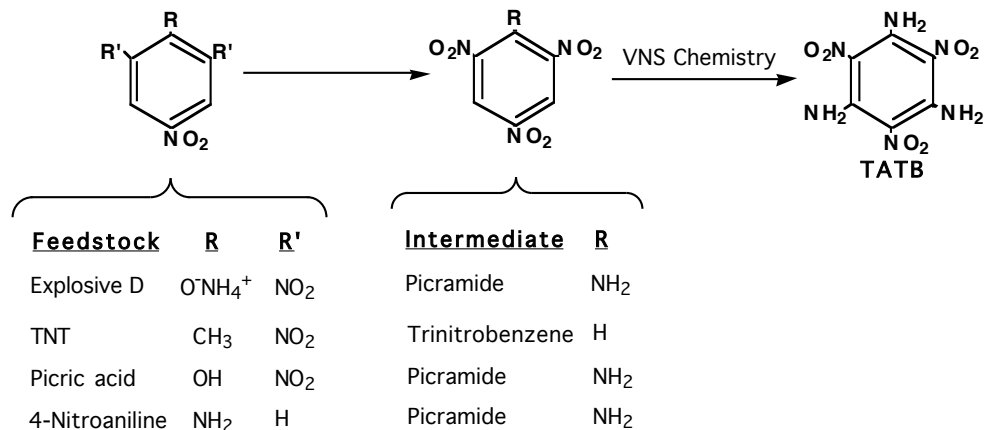


Figure 13. Conversion of nitroarene feedstocks to TATB.

nitrated⁴³ to furnish the picramide used in our VNS syntheses of TATB. The conversions in Figure 13 are readily executed on a laboratory scale (5-10 g). Needless to say, considerable process development is required to take a new bench-top process to production levels. Some of our process development studies will now be discussed.

PROCESS DEVELOPMENT STUDIES FOR TATB PRODUCTION

VNS Amination Reagents

We have reported the use of three reagents for the amination of picramide and TNB to TATB by Vicarious Nucleophilic Substitution (VNS) of hydrogen.³⁶⁻³⁹ The reagents in order of increasing reactivity, as well as increasing cost, are hydroxylamine, 4-amino-1,2,4-triazole (ATA) and 1,1,1-trimethylhydrazinium iodide (TMHI) (Figure 14). Hydroxylamine is an inexpensive chemical obtained in bulk quantities as the hydrochloride or sulfate salt.⁴⁴ ATA is obtained from formylhydrazide, which is prepared from relatively inexpensive hydrazine and ethyl formate (or formic acid).⁴⁵ TMHI is prepared from reaction of the more

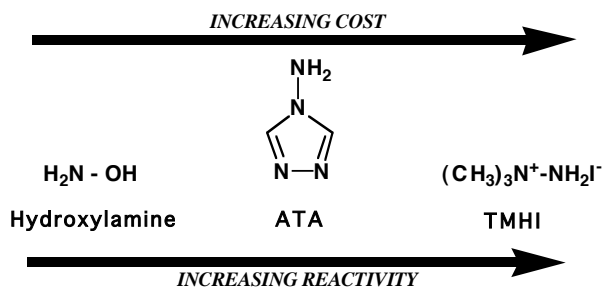


Figure 14. VNS amination reagents.

expensive 1,1-dimethylhydrazine and methyl iodide.³⁶ We have produced TMHI *in situ* by allowing 1,1-dimethylhydrazine and methyl iodide to react in DMSO. Subsequent addition of picramide and base produces TATB in yields comparable to VNS syntheses of TATB employing isolated TMHI.³⁹ We realized at the outset of our work with TMHI that methyl iodide, a relatively expensive halocarbon, would ultimately have to be replaced with a less expensive alkylating agent that was also halogen-free. We have demonstrated that dimethyl sulfate reacts with 1,1-dimethylhydrazine to produce 1,1,1-trimethylhydrazinium methosulfate (TMHM) *in situ* which reacts with picramide in the presence of base to produce TATB.³⁹ While the *in situ* production and use of TMHM in place of TMHI represents a significant cost reduction, the use of 1,1,1-trimethylhydrazinium salts in VNS reactions cannot compete economically with hydroxylamine or 4-amino-1,2,4-triazole (ATA) until there is a significant decrease in the cost of 1,1-dimethylhydrazine.

Reaction Condition Studies

Initially, the conversion of picramide to TATB was studied using inexpensive hydroxylamine and aqueous base as reported for the preparation of CL-14.²⁹ Only DATB was obtained (16%) after isolation from unreacted picramide. The conditions of the reaction were modified and the yield of DATB increased (90%), but still no TATB was produced (Figure 8). This reaction warrants additional study in light of the significant cost and environmental payoffs that accrue if VNS reactions producing TATB can be run in water, the ultimate inexpensive, “green” solvent. The combination of strong base, aprotic dipolar solvent (DMSO) and elevated temperature (65 - 90°C) forces the reaction of hydroxylamine with picramide to yield TATB in 50 – 74% yield with about 97% purity (Figure 15).³⁹

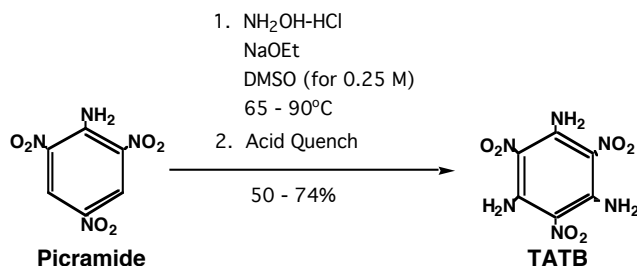


Figure 15. VNS synthesis of TATB using hydroxylamine hydrochloride.

We have shown that TMHI is the most efficient aminating reagent available for the VNS synthesis of TATB.³⁶⁻³⁹ Picramide, TMHI and base (sodium alkoxide or hydroxide) react in DMSO to provide TATB in 80 – 90% yield (Figure 16). The reaction is conducted at room temperature and is complete in less than 3 hours. Under these reaction conditions no DATB ($\leq 0.5\%$) is detected by FTIR spectroscopy or direct insertion solids probe mass spectroscopy (DIP-MS). The largest scale attempted thus far has been at the 50 gram level. While TMHI is very reactive and efficiently produces TATB, there are significant disadvantages to its use. The reagents used to generate TMHI (UDMH and methyl iodide) are toxic and

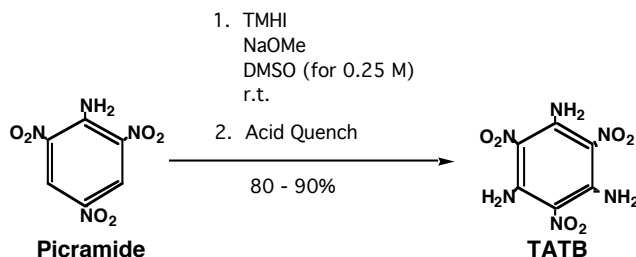


Figure 16. VNS synthesis of TATB using TMHI.

relatively expensive. In addition, the by-product of amination using TMHI is trimethylamine, a volatile and noxious gas which must be scrubbed from the reaction exhaust system. In contrast, hydroxylamine is much cheaper, less toxic and does not release gaseous products.

Product Analysis

TATB prepared from the VNS process will have to satisfy purity and testing profiles (DSC, CRT, DH_{50} , spark and friction tests, etc.) established for conventionally prepared TATB.¹⁰ FTIR and DIP-MS show TATB using TMHI and ATA is chemically $>99\%$ pure while the use of hydroxylamine gives TATB that is typically $>97\%$ pure. DSC (differential scanning calorimetry) values are $10 - 20^\circ\text{C}$ low for TATB prepared with hydroxylamine or TMHI. In addition, hydroxylamine or TMHI furnish TATB preparations that are tan to dark brown in color while pure TATB is typically yellow. In contrast, TATB prepared with ATA has good color and higher DSC values.

Use of Alternative Solvents in VNS Reactions

Most VNS reactions, with some notable exceptions (*vide supra*),^{28,29} employ dipolar aprotic solvents (DMSO, DMF, NMP) that are more expensive than most organic solvents used in industrial processes. While we have not been able to use water in the VNS production of TATB (Figure 8), we have been able to replace DMSO with less expensive solvents under certain conditions. The preliminary results are very encouraging and indicate a potentially significant cost reduction in the VNS production of TATB.

Purification of TATB

It is significant to note that TATB, unlike other high explosives (RDX, HMX, TNT, and HNS), cannot be purified using conventional techniques.¹⁰ The extremely low solubility⁴⁶ and involatility⁴⁷ of TATB precludes the use of recrystallization, chromatography and sublimation for large-scale operations. In the past, production batches of TATB that exceeded the allowable limits for ammonium chloride and/or other impurities had to be discarded. This is clearly economically and environmentally undesirable. We are developing a proprietary process for the purification of TATB. Our initial results have been encouraging as we have been able to remove DATB (resulting from incomplete amination of picramide) and a variety of low-level, deeply colored impurities. The process produces purified TATB with a particle size $\geq 20\ \mu\text{m}$ and is amenable to scale-up. Our goal is to reclaim rejected or substandard TATB, irrespective of source (synthesis, demilitarization activities).

SUMMARY AND CONCLUSIONS

We have described in some detail our progress in converting surplus energetic materials (Explosive D, picric acid) to TATB, a higher value explosive with civilian and military applications. Improved conversions of selected nitroarenes (picramide, TNB) to TATB using Vicarious Nucleophilic Substitution (VNS) chemistry bring us closer to a less expensive and more environmentally acceptable production of TATB. The scale-up of TATB production based on ongoing process development studies is in progress.

ACKNOWLEDGEMENTS

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. Funding for this work has been provided by the Joint DOD/DOE Munitions Technology Program, Munitions Life Cycle Technology R&D Program (Technology Coordination Group IX) with matching funds from the Advanced Development and Production Technology (ADAPT) Program. The continuing interest and support by James Q. Wheeler (US Army Operations Support Command, Rock Island, IL), Dr. Solim Kwak (Defense Ammunition Center, US Army, McAlester, OK) and Dan Burch (Naval Surface Warfare Center, Crane, IN) are gratefully acknowledged.

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